9 Optical properties of solid-liquid systems and the Casimir force

9.1 Summary

The force measurements presented in chapter 8 together with results reported in the literature, invited a more in-depth study on the applicability of oscillator models for liquids. Oscillator models are compared to available dielectric data of water and ethanol. The most important conclusion of this chapter is that the uncertainty in the measured dielectric data can lead to a very large scatter in theoretically predicted forces. In some cases it can reach a factor of two or 100% in the force. This is up to twenty times larger than that for gold surfaces in air, as reported in chapter 4, deeming the force calculations highly uncertain for these systems.

9.2 Introduction

Forces between solid surfaces immersed in liquid have been intensively studied in colloid physics **[1-19]**, where often water is used as the intervening medium **[4,5]**. Electrostatic double layer forces are present in many studies, and dispersion van der Waals (vdW) or Casimir forces are often approximated by the Hamaker theory **[3]**, which states that dispersion forces scale with distance as $F \sim d^{-2}$, e.g., in the sphere-plane configuration, at short separations. If, however, higher accuracy is necessary for the calculation of dispersion forces, one has to employ the Lifshitz theory **[2]**. In that case, the knowledge of the dielectric function is necessary for frequencies that span several orders of magnitude, e.g., from the far-infrared to extreme ultraviolet regime. For many materials this requirement is problematic since only limited or even no dielectric data are available. As a result many researchers today still use the Hamaker theory **[3]**, or the Ninham-Parsegian oscillator models **[6]** built from rather limited measured dielectric data **[7-11]**.

Generally it is assumed that the Lifshitz theory accurately predicts the magnitude of dispersion forces in liquids when the correct dielectric data are incorporated. However, besides the many approximations or uncertainties in the available dielectric data, precise validation of the Lifshitz theory in liquids (i.e. without fitting theory to force measurements) only recently started **[17-19]**. Therefore, knowledge of the intrinsic uncertainty of the force calculations is necessary. Another source of uncertainty is that dielectric data are obtained by different groups using different techniques **[12-14]**. In addition, variation in the dielectric data has been attributed to the quality of the material preparation. At any rate, variation in dielectric data results in an uncertainty in

the calculated forces using the Lifshitz theory, unless the dielectric properties of the specific materials used for the force measurements are also accurately measured over the full frequency range **[12]**.

Finally, it is known that the Lifshitz theory can predict relatively weak or repulsive dispersion forces between surfaces immersed in liquids **[15-19]**. Repulsive forces arise when for the dielectric functions $\varepsilon(i\zeta)$ (computed by the Kramers-Kronig relation at imaginary frequencies) of the surfaces 1 and 2 we have $\varepsilon_1(i\zeta) > \varepsilon_{liquid}(i\zeta) > \varepsilon_2(i\zeta)$ for all frequencies ζ. The force is attractive when this is not the case for all frequencies. When $\varepsilon_{liquid}(i\zeta) = \varepsilon_{surface}(i\zeta)$ for all frequencies ζ, then there is no force. Although in reality this will never be the case, for some finite frequency regime the dielectric function of the liquid is larger than that of one of the surfaces, $\varepsilon_{liquid}(i\zeta) > \varepsilon_{(1 \text{ or } 2)}(i\zeta)$, whereas in another regime the inverse may occur. This situation is exactly the case for the system silica-liquid-gold for which we will present Lifshitz theory calculations for multiple liquids with various degrees of knowledge of the dielectric functions.

9.3 Lifshitz theory for force calculations

For the force calculations we will use Lifshitz theory without the temperature correction **[2]**. At measurable plate-plate separations (*<500 nm*) the finite temperature corrections are insignificant **[20]**. Because the dielectric response of materials can change with temperature specifically in the microwave regime **[21]**, the dielectric data for all materials presented here are obtained at room temperature, where also the force measurements are performed **[17-19]**. For the sake of clarity, we will also ignore roughness corrections **[22]**.

In the Derjaquin (or Proximity Force) approximation the vdW/Casimir force for a sphere with radius R_{sph}=9μm (spheres used in chapter 8) and a plate, separated a distance L, is obtained from the the Casimir energy between parallel plates E_{pp} with area A unity as follows

$$F=2\pi R_{sph}E_{pp} \rightarrow E_{pp} = \frac{\hbar}{2\pi} A \sum_P \int \frac{d^2q}{(2\pi)^2} \int_0^\infty d\zeta \ln[1 - r_{31}^p r_{32}^p e^{-2\kappa_3 L}] \qquad \textbf{(9.1)}$$

where $r_{ij}(q,\zeta)$ are the reflection coefficients, $\boldsymbol{q}$ is the transverse wave vector (and q=|**q**|) and *p* distinguishes the two polarizations of the electromagnetic field (*TM* and *TE*). The reflection amplitudes $r^{p,s}_{3i}$ are given by the Fresnel reflection coefficients:

$$r_{3,i}^{TE} = \frac{\kappa_i - \kappa_3}{\kappa_i + \kappa_3}, \quad r_{3,i}^{TM} = \frac{\kappa_i \varepsilon_3(i\zeta) - \kappa_3 \varepsilon_i(i\zeta)}{\kappa_i \varepsilon_3(i\zeta) + \kappa_3 \varepsilon_i(i\zeta)} \text{ and } \kappa_i = \sqrt{q^2 + \frac{\varepsilon_i(i\zeta)\zeta^2}{c^2}} \qquad \textbf{(9.2)}$$

where $\varepsilon_{1,2}$ denote the dielectric functions for the surfaces, and ε_3 is the dielectric function for the liquid.

The reflection amplitudes depend on the dielectric function at imaginary frequencies $\varepsilon(i\zeta)$, which is obtained by the Kramers-Kronig analysis of the measured imaginary part $\varepsilon''(\omega)$ of the real dielectric function $\varepsilon(\omega)$

$$\varepsilon(i\zeta)=1+\frac{2}{\pi}\int_0^{+\infty} d\omega \frac{\omega\varepsilon''(\omega)}{\omega^2+\zeta^2}. \qquad \textbf{(9.3)}$$

For all our materials, we obtained the dielectric function at imaginary frequency by direct numerical integration of the imaginary part of the dielectric function. This procedure is allowed because the dielectric data are available over a sufficiently large range of frequencies.

Since we will frequently refer to the Ninham-Parsegian oscillator models **[6]** for comparison to real dielectric data, their definition will be briefly presented here. In fact, oscillator models are constructed to represent the dielectric function at imaginary frequencies, in the case when there is little or no knowledge of the dielectric function of a substance. The form of the oscillator model is given by

$$\varepsilon(i\zeta)=1+\sum_i \frac{C_i}{1+(\zeta/\omega_i)^2}. \qquad \textbf{(9.4)}$$

The coefficient C_i is the oscillator strength at a given (resonance) frequency ω_i. Typically two or three oscillator functions are used, namely, an ultraviolet (UV) part, infrared (IR) part, and sometimes a microwave (MW) part (though its form can be slightly different from the typical dependence $\sim(\zeta/\omega_i)^2$ in Eq. (9.4) **[8]**). The sum of C_i's should always satisfy the relation $\sum C_i = \varepsilon_0 - 1$ with ε_0 the static dielectric constant of the substance.

We calculate the force using basic numerical integration. The input is either measured dielectric data at imaginary frequencies or an oscillator model. For accurate calculations with Lifsitz theory it is enough to perform the integration in the frequency range 0.001eV-100eV.

9.3 Accuracy of the force calculations for specific systems

It is known that the variation of the dielectric functions, e.g., for gold, can be rather large because of defects and grains (depending on the manufacturing process) in the material. This may lead to a variation in vdW/Casimir force of *5-15%* as calculations in terms of the Lifshitz theory for gold surfaces in air indicated **[12]**. Obviously for other materials we may expect similar behavior.

In fact, for silica the variation in the dielectric functions are due to variations in density and water content **[13]**. For liquids, besides system temperature, also the purity plays a significant role on their dielectric response **[14]**. Therefore, assuming that the Lifshitz theory, Eq. (9.1), is accurate (which is not uncontroversial since there may be issues regarding the range of validity of the underlying electromagnetic stress tensor inside material media that goes into the force theory derivation), scatter in the dielectric data as input for the force calculations is the only significant source of error.

For gold, silica, and water the dielectric functions are well known and measured by various groups. We will use two sets of data for gold as published in ref **[12]**. Also two sets of data will be used for silica as obtained by different groups **[13]**. Finally, for water we will use the data of Segelstein **[14]**, and an *11-order* oscillator model **[11]** that has been fit to different sets of data **[7,9]**. All the dielectric data are shown in Fig. 9.1, which depicts significant scatter in dielectric data for all materials.

Fig. 9.2 shows the calculated forces using Lifshitz theory for the different sets of dielectric data. Here we would like to emphasize the following. Although in the case of silica one of the data sets has significantly less data points in the visible and near infrared (IR) range, this is not the reason for the different outcome in the force calculations. This is because the major adsorption peaks (UV and IR range), which define the dielectric function at imaginary frequencies and the calculated forces, contain sufficient data points. Furthermore, the scaling of the force with distance in Fig. 9.2c is defined as $scaling=|(-log_{10}(|F_i|)+log(|F_{i-1}|)) / (log(X_i)-log(X_{i-1}))|$ where F_i and X_i represent force and separation for successive data points i, respectively.
Surprisingly, for the gold-water-silica system the scatter in the dielectric data leads to scatter in the calculated forces, which reaches the level of *60%* for separations $L<500\ nm$. This scatter is much larger than the variation in the force between gold surfaces in air. Therefore, unless the dielectric properties of the specific samples used in force measurement are measured over a very large frequency range, any comparison of force measurements in liquid to Lifshitz theory predictions is only meaningful as a rough estimate (i.e. within *~50%* error bars).

The reason for these dramatic effects originates from the fact that the magnitude of the dielectric functions at imaginary frequencies for water and silica are similar for most frequencies. Indeed, in the range 10^{-2}-$10^{2}\ eV$ the difference is of the order of *30%* or less, which is in fact similar in magnitude to the scatter of the measured dielectric functions. To illustrate this effect we present calculations for silica-water-silica and gold-water-gold in Fig. 9.3. Besides the fact that in the case of silica the force has decreased to below force resolution level of a typical AFM colloid probe system (the force is less than *10 pN* at separations $L\geq 10\ nm$), the scatter in the force calculations

becomes very large, e.g., *100%* for silica compared to *18%* for gold. Therefore, the accuracy of the force calculations for the systems described in **[17]** and **[18]** is rather low, while in **[19]** the accuracy of the force calculations can be better. Nonetheless, in all these cases **[17-19]** oscillator models were used for the liquids, which contribute to inaccuracy of the calculations as will be shown in the following.

9.4 Oscillator models for representing the dielectric function

9.4.1 The case of water

The accuracy of the force calculation will further deteriorate if poorly constructed oscillator models are used to represent the dielectric response of liquids. The problem for most liquids, except water, is that the dielectric function is not well known **[6-11]**. As a consequence, it is understandable that oscillator functions **[6, 7]** are constructed from the limited available measured dielectric data to obtain an approximate dielectric function at imaginary frequencies for a specific liquid **[8]**. For example, sometimes the dielectric strength measured at only a few fixed frequencies (e.g., the sodium D line) was used to determine the strength of an oscillator **[8]**.

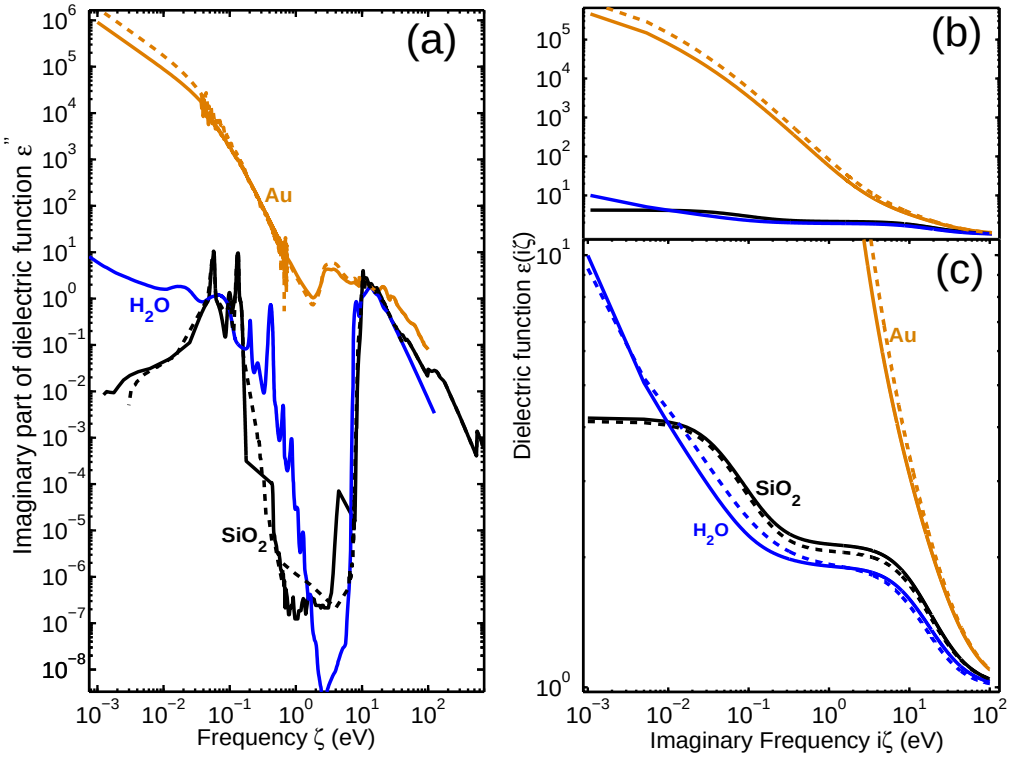

Figure 9.1: (a) *Raw dielectric data of Au, H_2O and SiO_2 obtained from different references.* ***(b)*** *Dielectric functions at imaginary frequencies.* ***(c)*** *is a magnification of* ***(b)*** *showing better the differences between water and silica. The solid and dashed lines for silica and gold are 2 different sets of optical data. For water the solid line corresponds to the data from Ref.* ***[14]****, and the dashed line is an 11-order oscillator model which has been fitted to a different set of optical data.*

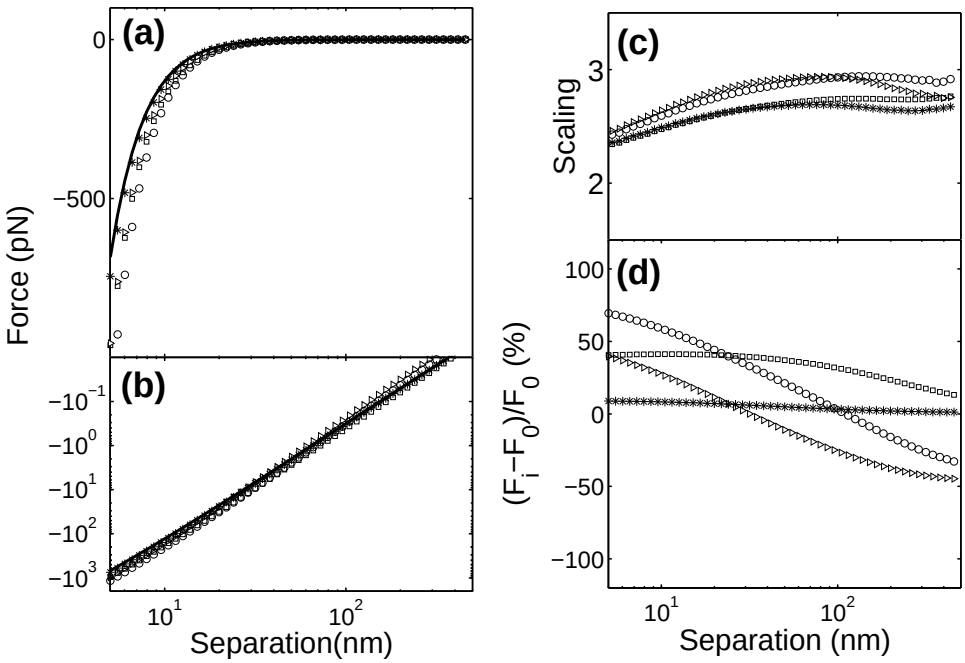

Figure 9.2: *Calculations of the Casimir force for the different sets of data. The solid line is the reference line. Circles, squares, triangles and stars are calculations when we interchange one set of dielectric data with another set for one or more materials. (The upper two graphs show the force in linear* ***(a)*** *and log scale* ***(b)*** *with distance.* ***(c)*** *Scaling of the force with distance z as defined in the text. Clearly squared to cubed scaling, e.g. from non-retarded to retarded regimes is observed.* ***(d)*** *The relative difference in force as compared to the reference force in percent.*

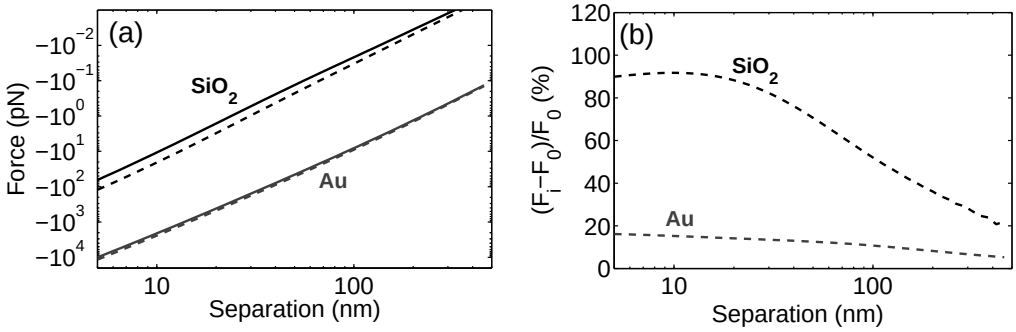

Figure 9.3: ***(a)*** *Lifshitz theory calculations for gold-water-gold and silica-water-silica.* ***(b)*** *Relative difference in percent of the force when different measured dielectric data sets (as shown in Fig. 9.1) for gold, and glass are used. For gold the effect on the force is small, whereas for silica it is very large because its dielectric function is similar to water.*

Since for water the dielectric function is known, we can make a comparison to oscillator functions provided in **[10]**. Fig. 9.4 shows that the difference with the real data is very large. In particular the dielectric strength in the UV regime is underestimated, and in the IR regime it is rather overestimated. The effect on the resulting force in the non-retarded (or vdW) regime is not large. Indeed, the force is about *25%* times larger for separations < *10 nm*. However, in the retarded regime the force becomes

even repulsive for separations *L>25 nm*. It should be noted, however, that the oscillator models in **[7, 9]** reproduces the dielectric data by Segelstein **[14]** rather well.

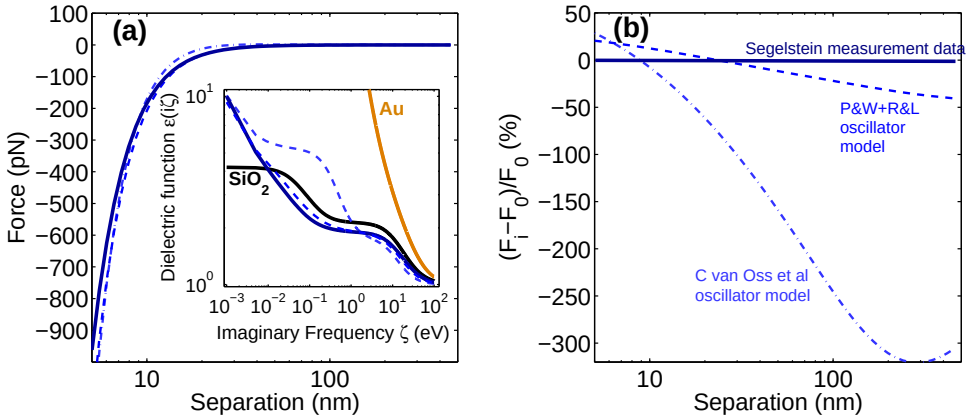

Figure 9.4. *Lifshitz theory for gold-water-silica. Here we calculate the force using real measured data by Segelstein, and oscillator models, one from ref.* ***[10]*** *(van Oss et al.), and one from refs* ***[7]****,* ***[9]*** *and* ***[11]****. The force is shown in linear scale* ***(a)****. The inset in (a) shows the dielectric functions of all materials and the various oscillator models for water. In* ***(b)*** *we show relative differences in percent (%) for the various oscillator models as compared to the data in* ***[14]****.*

One can argue that the other oscillator model as constructed by van Oss et al. **[10]** (where the same parameter values for water can be found in **[6, 8]**) is highly inaccurate. Nonetheless, probably the large difference in the dielectric strength in the IR regimes can be attributed to average values obtained from a limited data set around the IR regime. Notably, in those days there was not much focus on IR parameters since the UV parameters were of paramount importance for the non-retarded Hamaker constants. This is also one of the reasons why the oscillator model in **[6, 10]** still works relatively well below *10 nm*.

9.4.2 The case of ethanol

The measured dielectric function for ethanol presented here was constructed over a very wide range of frequencies from real measured data provided in existing literature (Fig. 9.5). We will compare force calculations using this data to force calculations based on the oscillator models for ethanol that have been used for comparison to measurements in **[19]** where the model of Milling et al. **[16]** was used for force calculations. For the measurements in **[18]** the three oscillator model of van Oss et al. **[10]** was used for the force calculations.

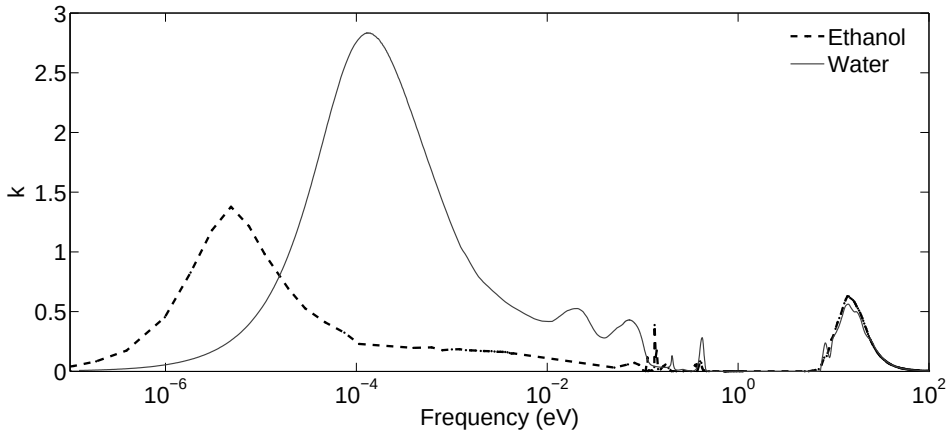

Figure 9.5. *The extinction coefficient for ethanol over a wide range of frequencies from refs.* ***[23]-[27]****. With the Kramers-Kronig relations the dielectric function at imaginary frequencies can be obtained from this graph. For comparison we also show the extinction coefficient for water* ***[14]****. All data are shown in semi-log scale.*

The dielectric function for ethanol was constructed as follows. The millimeter range was taken from **[23]**, the micrometer range from **[24]**, the mid infrared range from **[25]**, the near infrared range from **[26]**, and the ultraviolet and x-ray range from **[27]**. Only in the visible and in the far infrared range some data are still lacking. However in the visible range ethanol is transparent (very low extinction coefficient, which can be assumed to be zero in our case), and therefore this part will not contribute to the dielectric function at imaginary frequencies. The far-IR regime may have some features, but we do not expect order of magnitude changes from the linear interpolation in this range. In any case the lack of knowledge of the dielectric function in this range will not give a large contribution for the calculated forces in the ranges considered here (<*500 nm*). On the other hand, the UV part will have the predominant role in the calculation of the force at smaller ranges, and for this part we have reliable data **[27]**. Although in the literature a significant spread exists in the measurements of dielectric data $\varepsilon(\omega)$ for ethanol **[27]**, we derived a fairly accurate dielectric function $\varepsilon(i\zeta)$ by means of Eq. (9.3).

The results of the calculated forces for silica-ethanol-gold are shown in Fig. 9.6. Although the oscillator model of Milling et al. **[16]** for ethanol predicts repulsive forces over all ranges, attractive forces were measured **[18]**. The three oscillator model of van Oss et al. **[10]** shows a better agreement with the forces obtained from measured dielectric data for ethanol, but it predicts slightly weaker forces. The force measurements in **[18]** are in reasonable agreement with the calculated forces obtained with the full measured dielectric spectrum of ethanol (deviations within *50 %* over most ranges, see also Fig. 9.8). In particular for this system the scatter in the theory is of the order of *50-100%* or a factor of 2 when using different sets of measured

dielectric data. Therefore, we can conclude that they are consistent at that level of accuracy.

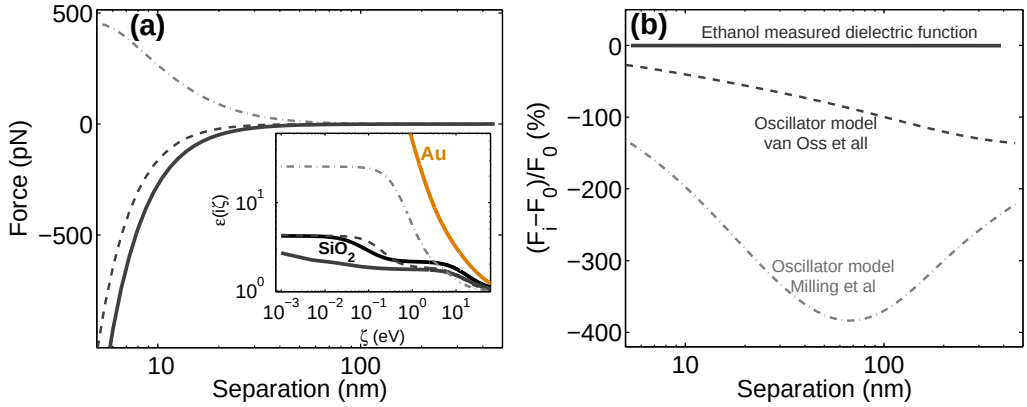

Figure 9.6. ***(a)*** *Calculated forces for gold-ethanol-silica using measured dielectric data for gold, silica and ethanol. We compare the latter to force calculations based on the oscillator models of the dielectric function for ethanol from* ***[10]*** *and* ***[16]****. The inset shows the dielectric function of gold silica and ethanol together with those of the two oscillator models for ethanol.* ***(b)*** *The relative difference in force for the two oscillator models as compared to the forces obtained from measured dielectric data (used as reference: F_0). The model of van Oss et al.* ***[10]*** *is relatively accurate (within a factor 2 for separations < 100 nm), while the model of Milling et al.* ***[16]*** *predicts repulsive forces.*

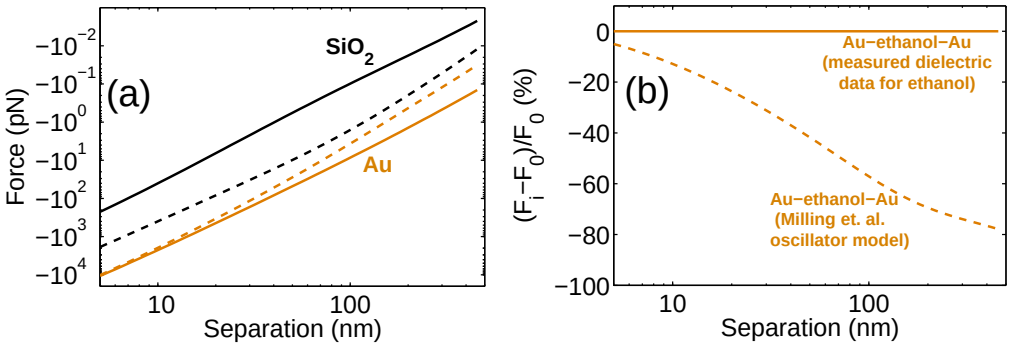

Figure 9.7. *(Right)* ***(a)*** *Calculated forces for gold-ethanol-gold (orange lines) and silica-ethanol-silica (black lines). The solid data are obtained with measured dielectric data for ethanol. The dashed line is obtained with the oscillator model of Milling et al.* ***[16]****. The differences are extremely large in the case of silica were the oscillator model predicts forces more than an order of magnitude too large.* ***(b)*** *For gold-ethanol-gold the situation is better, but still the forces are underestimated by 10-80 %.*

In Fig. 9.7 data are shown for silica-ethanol-silica and gold-ethanol-gold. In the case of silica-ethanol-silica the oscillator model of Milling et al. **[16]** predicts forces which are more than an order of magnitude too large. For gold-ethanol-gold force measurements were found to be in agreement with the model of Milling et al. **[16]** in the range *20-100 nm* **[19]**. Therefore, it is worthwhile to compare this model to the real dielectric data for this system. It appears that when using this model in the range *20-100 nm* the forces are

underestimated by *30-60 %* in the range *20-100 nm*. But given the large scatter in the measured forces in **[19]**, we feel that this experiment was not accurate enough to be sensitive to these differences **[19]**. Moreover, also in that case we can conclude that the measurements in **[19]** are in reasonable agreement with the correct theory within roughly *30-50 %* uncertainty.

The poor quality of the oscillator model by Milling et al. **[16]** stems from the fact that they assumed that there was no significant absorption in the microwave regime. As a result they gave an IR oscillator with high strength because their model must satisfy $\sum C_i = \varepsilon_0 - 1$. This argument is unphysical since polar liquids such as water and ethanol absorb strongly in the microwave region as described by the Debye relaxation. The Debye term is included in the model of van Oss et al. **[10]**, which is the reason why their model gives somewhat better results. Therefore, it is of no surprise why Milling et al. **[16]** appear to have found erratic behavior (attractive forces) when they measured forces between teflon and gold surfaces in ethanol.

9.5 Theory and experiment

For the sake of completeness we now compare all calculations to force measurements for the gold-ethanol-silica system **[18]** for which we initially expected repulsive forces based on the model of Milling et al. **[16]**. Multiple dielectric data were used for gold and silica. For ethanol the dielectric data are varied by *15%* in the UV regime (see **[27]** for the variation in absorption measurements in the UV regime). For all materials there is roughly *10-30 %* variation in the measured dielectric data. When oscillator models are used for ethanol, then we use only one data set for gold and silica.

From figure 9.8 it is clear that the measured force data follow the full theory showing similar scaling with distance. However, the scatter in the theory is very large, and only accurate within a factor of two (or equivalently *100 %*). When the model of van Oss. et al.**[10]** was used for ethanol, the discrepancy between theory and measurements becomes larger for bigger separations. Note that any discrepancies between the different calculations and the force measurements at the smallest ranges (*<10nm*) can be explained by the uncertainty in the measured distance (~1nm). At the largest ranges the error in distance leads to smaller uncertainty in the measured forces. Clearly the oscillator model of Milling et al. **[16]** even fails to predict the sign of the force.

Summarizing the results for water and ethanol we can infer that oscillator models are not suitable for precision calculations using the Lifshitz theory. The prime reason for their use was the ability to construct dielectric functions at imaginary frequencies, while only having limited experimental data. In that sense, these models are only useful to obtain a rough estimate of

the force, e.g. within an order of magnitude, unless they are built around dielectric data for the VUV and IR frequency ranges.

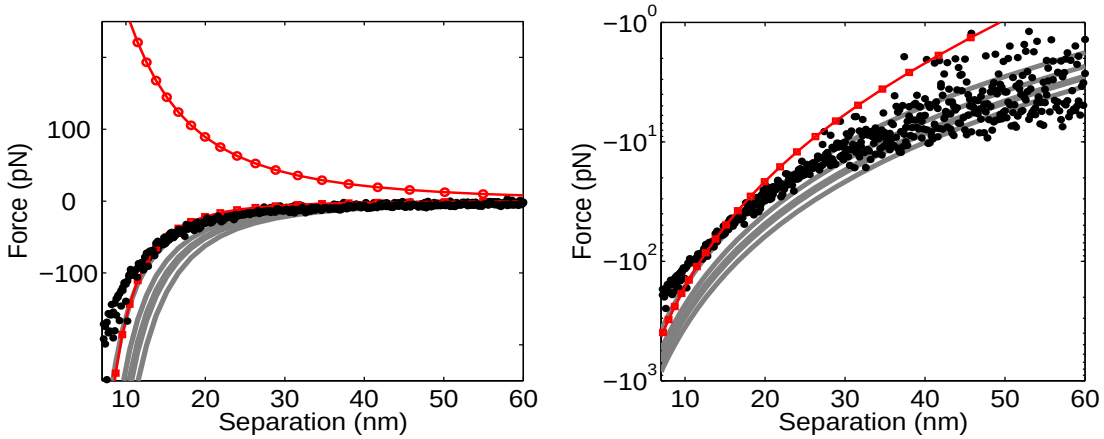

Figure 9.8. *Force measurements (black circles: force average of many spheres from chapter 8), plotted on linear and semi-log scale for the gold-ethanol-silica system, compared to theory using multiple dielectric data sets for gold, ethanol, and silica (Grey solid lines). A comparison with two oscillator models for ethanol is made, the one of van Oss et al. (red squares)* ***[10]*** *and the one of Milling et al. (red circles)* ***[16]****. Clearly the measurements coincide best with a set of the full theory.*

9.7 Conclusions

We have shown in this chapter that the scatter in the measured dielectric data of solid materials and liquids can lead to a large scatter of up to a factor of two and possibly more in the calculated vdW/Casimir force as obtained by Lifshitz theory. This particularly happens in the case when the dielectric functions of the liquid and one of the interacting surfaces become comparable in magnitude. Oscillator models built around very limited dielectric data lead to even worse results, underlining the importance of using accurate dielectric data in Lifshitz theory.

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